Computational Modeling of Oxidation Catalysis

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2008

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Summary

In this thesis, several reactions and reactants that take part in the Fenton reaction have been studied using theoretical calculations, namely DFT calculations and Car-Parrinello simulations. The Fenton reaction is a very elegant and environmentally friendly way to oxidize organic substances using Fe^{2+} ions and hydrogen peroxide (H_2O_2) in water, and has been known since the late 19th century. However, the mechanism by which the Fenton reaction occurs is not completely known, and there has been a long-lasting debate on the subject.

Fenton's reagent is a rather strong but unspecific oxidation catalyst, and its main use is found in the oxidation of wastewater, besides several other industrial applications. Increased knowledge of the mechanism of the Fenton reaction may open the way to development of more specific catalysts based on Fenton's reagent, that share its advantages (being strong and environmentally friendly).

In Chapter 1, we have discussed the debate on the mechanism of the Fenton reaction, which is focused on whether the active intermediate is $OH^{\bullet}$ or FeO^{2+}. In this discussion, usually also other oxidants than H_2O_2 (like HOCl, ROOH, and ROOR) and other solvents than water are incorporated, assuming identical chemistry in all these cases. We have pointed out, though, that most probably the mechanism is different in different systems and may depend on the nature of reactants, the concentration of reactants, the solvent, presence of molecular oxygen, presence of light, and other variables. These variables determine whether the reactive intermediate is $OH^{\bullet}$, FeO^{2+}, or perhaps both. For the system with Fe^{2+} and hydrogen peroxide in water, simulations of Ensing et al. have shown that FeO^{2+} is the active intermediate and $OH^{\bullet}$ is formed only very shortly and not as a free reactant.

In this thesis, we have studied (1) the behavior of an $OH^{\bullet}$ radical in water and whether or not it can diffuse via a Grotthuss diffusion mechanism; (2) the mechanism of the reaction of FeO^{2+} with methanol in water; (3) the influence of water on the reactivity of FeO^{2+}; and (4) the influence of ligands on the reactivity of FeO^{2+}, focusing on the different effects of equatorial and axial ligands.

Before going into the calculations themselves, we have discussed some technical aspects for the simulations in Chapter 2. Firstly, we have discussed the Car-Parrinello method and a recent debate on what should be the best values for the fictitious mass and the timestep in this method. We have shown that it is better to use a much smaller fictitious mass than commonly used and that nevertheless a large timestep can be used. Secondly, we have discussed the Projector Augmented Wave (PAW) method, which we have used in order to obtain an efficient description of the iron ions. The theory *and* the weaknesses of this method are shortly explained, and we have optimized sets of PAW projectors such as to obtain acceptable results for our type of systems. Thirdly, we have given a derivation of the virial equation for calculating the pressure in molecular simulations. We have shown that this equation

does not hold in extended systems when non-pair-additive models are used. Sadly, this means that we have not been able to monitor the pressure in our simulations.

In Chapter 3, the behavior of $OH^{\bullet}$ radicals in water solution has been studied. We have found that, when the BLYP functional is used, $OH^{\bullet}$ makes an O–O hemibond with one of the surrounding waters. This hemibond occupies the unpaired electron of $OH^{\bullet}$ and blocks H atom transfer from surrounding water molecules, making rapid diffusion of $OH^{\bullet}$ via a Grotthuss mechanism unlikely. Although the abundance of the hemibond is believed to be overestimated by the BLYP functional, simulations with corrected models confirm that no hydrogen bonds are formed with the unpaired electron and only very slow Grotthuss diffusion has been observed for the $OH^{\bullet}$ radical.

In Chapters 4, 5, and 6 we have studied the FeO^{2+} species. In Chapter 4, the oxidation of methanol to formaldehyde by $[FeO(H_2O)_5]^{2+}$ has been studied, using both gas phase calculations and simulations in water. We have found that FeO^{2+} attacks specifically at the C–H bond abstracting an $H^{\bullet}$ atom. Subsequently, the OH hydrogen of methanol transfers to the iron complex spontaneously, completing the reaction. Interestingly, in the gas phase the barrier for the first hydrogen abstraction is only a mere 2 kJ/mol, while in solution a free energy barrier of 50 kJ/mol (upper bound) was found. Such a difference was also found before for the oxidation of methane to methanol.

In Chapter 5, the unexpectedly large solvation effects on hydrogen abstraction by FeO^{2+} were further studied by way of an electronic structure analysis. FeO^{2+} turns out to be extremely electrophilic because of a very low-lying $3\sigma^{*\uparrow}$ LUMO. C–H bonding orbitals are slightly higher in energy than this $3\sigma^{*\uparrow}$ LUMO of FeO^{2+}, which causes a large charge donation activating the C–H bond. In water solution, however, the orbitals shift upwards in energy and the difference between the FeO^{2+} and C–H orbitals changes, diminishing the all important charge transfer interaction. This is a very unusual type of solvent effect that opens a way to control the reactivity of FeO^{2+}.

In Chapter 6, we have continued the investigation of how the reactivity of FeO^{2+} complexes can be controlled via their $3\sigma^{*\uparrow}$ orbitals. In this chapter the effect of ligands was investigated and explained by their effect on the $3\sigma^{*\uparrow}$ orbital. We have stressed that the $3\sigma^{*\uparrow}$ orbital is only the important orbital when the system is in a high spin state, which is favored when the equatorial ligands are only weakly σ-donating. Once the high spin ($S = 2$) is guaranteed by a judicious choice of the equatorial ligands, the reactivity can be further controlled by varying the *axial* ligand. Strong σ-donating ligands on the axial position destabilize the $3\sigma^{*\uparrow}$ and decrease its reactivity. Weak σ-donating ligands or an empty place increase the reactivity. Thus, a method has been found to control the reactivity of high-spin FeO^{2+} complexes, both via the solvent and the ligands. Hopefully, these results will accelerate the development of new catalysts based on FeO^{2+} complexes.